PATENT ABSTRACTS OF JAPAN

(11)Publication number : **06-166652**
(43)Date of publication of application : **14.06.1994**

(51)Int.Cl.

C07C 45/45
B01J 31/12
C07B 41/06
C07C 49/17
C07C 49/245
C07C 49/497
C07C 49/743
C07C 49/747
C07C 49/753
C07C 49/82
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C07C253/30
C07C255/17
C07C255/19
C07C255/40
C07D213/50
C07D311/94
// C07B 61/00

(21)Application number : **04-061545**
(22)Date of filing : **17.02.1992**

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(30)Priority

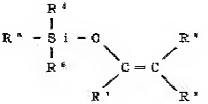
Priority number : **03313711** Priority date : **31.10.1991** Priority country : **JP**

(54) PRODUCTION OF ALDOL COMPOUND

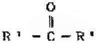
(57)Abstract:

PURPOSE: To obtain the subject compound useful as an intermediate for pharmaceuticals, agrichemicals, etc., in a state to enable easy reuse of catalyst by reacting a silyl enol ether with a carbonyl compound in the presence of a lanthanoid catalyst.

CONSTITUTION: The objective compound of formula III (Z is H or SiR4R5R6) can be produced by reacting a compound of formula I (R1 is H, alkyl, alkenyl, aryl or thio; R2 and R3 are H, halogen, nitro, cyano, alkyl, etc.; R4 to R6 are H, alkyl, alkoxy or aryl) with a compound of formula II (R7 and R8 are H, alkyl, acyl, alkenyl, etc.) in the presence of a compound of the formula Ln(OSO2 Rf)3 (Ln is lanthanoid; Rf is perfluoroalkyl or perfluoroalkoxy) in a protonic solvent (e.g. water-ethanol) at 0-150°C. A highly selective aldol condensation reaction can be applied to a wide variety of carbonyl compounds including formaldehyde and the used catalyst can easily be recovered and reused.



I



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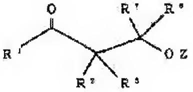


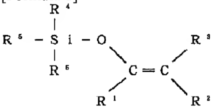
III

CLAIMS

[Claim(s)]

[Claim 1]A following general formula (1)

[Formula 1]



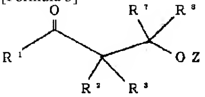
(1)

however, the inside of a formula and R^1 -- a hydrogen atom, an alkyl group, and an alkenyl group. Are an aryl group or a thio group, and R^2 and R^3 A hydrogen atom, A halogen atom, a nitro group, a cyano group, an alkyl group, an alkenyl group, an aryl group, It is an alkoxy group, an acyloxy group, an oxycarbonyl group, or an aminocarbonyl group, and R^1, R^2 or R^2, and R^3 are united, and may form a part of cyclic structure. R^4, R^5, and R^6 And a hydrogen atom, an alkyl group, are an alkoxy group or an aryl group, and any two and Si of these R^4, R^5, and R^6 are united -- cyclic structure -- it may form -- the silyl enol ether expressed and a following general

formula (2)
[Formula 2]

$$R^7-\overset{\overset{\displaystyle O}{\|}}{C}-R^8 \qquad (2)$$

It is a following general formula (3) about the carbonyl compound expressed with (however, are a hydrogen atom, an alkyl group, an acyl group, an alkenyl group, or an aryl group, these R^7 and R^8 are united, and R^7 and R^8 may form a part of cyclic structure among a formula).
$Ln(OSO_2Rf)_3$ (3)
The following general formula (4) making it react under existence of the lanthanoid series catalyst expressed with (however, the inside of a formula and Ln are lanthanoids atoms, and R_f is a perfluoro-alkyl group or a perfluoro-alkoxy group)
[Formula 3]



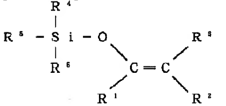
(4)

(However, Z is a hydrogen atom or a $-SiR^4R^5R^6$ group among a formula.) and R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 -- the above -- it is the same -- the manufacturing method of an aldol compound with which it is expressed.
[Claim 2]A manufacturing method of the aldol compound according to claim 1 reacting under protic solvent coexistence.
[Claim 3]A manufacturing method of the aldol compound according to claim 1 or 2 characterized by carrying out a reuse as a reaction catalyst without collecting as solution lanthanoid series catalysts used as a catalyst after ending reaction, isolating or isolating this catalyst from this collected solution.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the new manufacturing method of an aldol compound useful as synthetic intermediate, such as medicine and agricultural chemicals.
[0002]
[Description of the Prior Art]About the manufacturing method of the aldol compound, what is called aldol condensation that makes two kinds of carbonyl compounds react under the catalyst of acid or a base is known. [For example, refer to H.O.House"Modern Synthetic Reactions"2nd. and W.A.Benjamin and California (1972).] .
[0003]This aldol condensation as a method of advancing a high selection target in recent years, One carbonyl compound is once changed into silyl enol ether, the method to which this and the carbonyl compound of another side are made to react by the Lewes acid catalyst is developed, and various kinds of optically active substances are stereoselectively compounded as the

application. [aT.Mukaiyama, KNarasaka, KBanno, Chem.Lett., p1011(1973);bT.Mukaiyama, KBanno, KNarasaka, J.Am.Chem.Soc., 96, p7503. (1974);cS.Kobayashi, H.Uchino, Y.Fujishita, I.Shiina, T.Mukaiyama, J.Am.Chem.Soc., 113, p4247 (1991)] .Although the method of going via this silyl enol ether uses the Lewes acid catalyst, if a protic solvent like water or alcohol lives together, the Lewis acid known conventionally will react to this, and will lose that catalyst ability. Therefore, it becomes indispensable to perform a reaction in a non-solvent or an aprotic solvent. For this reason, in the non-solvent or the aprotic solvent, application of this method was difficult to the unstable carbonyl compound like formaldehyde.
[0004]In this method, after ending reaction, in order to separate a resultant and the Lewes acid catalyst, the reaction mixture is usually processed with water. That is, the Lewes acid catalyst was made to react to water, and it has changed and separated into water soluble matter. However, it was dramatically difficult to reproduce the Lewes acid catalyst from this water soluble matter, and also when discarding, the cleanup cost increased, and methods for manufacturing in large quantities industrially included the difficulty.
[0005]
[Problem(s) to be Solved by the Invention]Then, the result of having repeated research wholeheartedly this invention person solving various problems in the manufacturing method of this conventional aldol compound, It found out becoming a good catalyst at the time of a certain kind of lanthanoid series compound making silyl enol ether and a carbonyl compound react, and manufacturing an aldol compound, and this invention was completed. That is, the purpose of this invention is to provide the manufacturing method of a new aldol compound without a problem [as / in the conventional method mentioned above]. The purpose of this invention is to provide the manufacturing method of the aldol compound which can collect easily the catalysts which could be applied also to the unstable carbonyl compound in the non-solvent or the aprotic solvent, and were used, for example like formaldehyde, and can carry out a reuse.
[0006]
[Means for Solving the Problem]This invention is a following general formula (1).
[Formula 4]

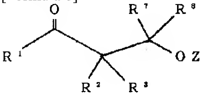


(1)

however, the inside of a formula and R^1 -- a hydrogen atom, an alkyl group, and an alkenyl group. Are an aryl group or a thio group, and R^2 and R^3 A hydrogen atom, A halogen atom, a nitro group, a cyano group, an alkyl group, an alkenyl group, an aryl group, It is an alkoxy group, an acyloxy group, an oxycarbonyl group, or an aminocarbonyl group, and R^1, R^2 or R^2, and R^3 are united, and may form a part of cyclic structure. R^4, R^5, and R^6 And a hydrogen atom, an alkyl group, are an alkoxy group or an aryl group, and any two and Si of these R^4, R^5, and R^6 are united -- cyclic structure -- it may form -- the silyl enol ether expressed and a following general formula (2)
[Formula 5]

$$R^7-\overset{\displaystyle O}{\overset{\|}{C}}-R^8 \qquad (2)$$

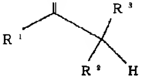
It is a following general formula (3) about the carbonyl compound expressed with (however, are a hydrogen atom, an alkyl group, an acyl group, an alkenyl group, or an aryl group, these R^7 and R^8 are united, and R^7 and R^8 may form a part of cyclic structure among a formula).
$Ln(OSO_2Rf)_3$ (3)
The following general formula (4) made to react under existence of the lanthanoid series catalyst expressed with (however, the inside of a formula and Ln are lanthanoids atoms, and R_f is a perfluoro-alkyl group or a perfluoro-alkoxy group)
[Formula 6]



(4)

(However, Z is a hydrogen atom or a $-SiR^4R^5R^6$ group among a formula.) and R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 -- the above -- it is the same -- it is a manufacturing method of an aldol compound with which it is expressed.
[0007]This invention is a manufacturing method of an aldol compound which performs a reaction of silyl enol ether (1) and a carbonyl compound (2) under protic solvent coexistence. In a method of this invention making aforementioned silyl enol ether (1) and a carbonyl compound (2) reacting under existence of a lanthanoid series catalyst (3), and manufacturing an aldol compound (4), It is a manufacturing method of an aldol compound which carries out a reuse as a reaction catalyst, without collecting lanthanoid series catalysts (3) as solution after ending reaction, isolating or isolating this catalyst from this solution.
[0008]In the above-mentioned general formula (1), (2), and (4), R^1, R^2, As an alkyl group used as R^3, R^4, R^5, R^6, R^7, and R^8, Substitution or an unsubstituted methyl group, an ethyl group, a propyl group, a butyl group, an isobutyl group, t-butyl group, an octyl group, dodecyl, etc. can be illustrated extensively. As an alkenyl group used as R^1, R^2, R^3, R^7, and R^8, substitution or an unsubstituted ethenyl group, a propenyl group, a butenyl group, etc. can be illustrated. As an aryl group used as R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8, Substitution or an unsubstituted phenyl group, a tolyl group, a naphthyl group, a pyridyl group, a thienyl group, a furil group, a pyrrolyl group, etc. are illustrated.
[0009]In the above-mentioned general formula (1), mentioning an alkylthio group like a methylthio group, an ethyl thio group, and t-butyl thio group, an aromatic thio group like a phenylthio group, a tolyl thio group, a naphthyl thio group, and a pyridyl thio group, etc. as a thio group used as R^1 cuts. R^1, R^2 or R^2, and R^3, Although these are united and a part of cyclic structure may be formed, as such cyclic structure, substitution or an unsubstituted cyclohexene ring, a cyclopentene ring, a cyclohexane ring, a cyclopentane ring, a cyclohepten ring, etc. can be illustrated. As an alkoxy group used as R^4, R^5, and R^6, a methoxy group, an ethoxy basis, a butoxy group, etc. can be mentioned as an example. Although any two and Si of R^4, R^5, and R^6 are united and cyclic structure may be formed, as an example, silacyclo alkane ring structures, such as a silacyclo pentane ring and a silacyclo hexane ring, can be mentioned.
[0010]In the above-mentioned general formula (2), as an acyl group used as R^7 and R^8, substitution or an unsubstituted formyl group, An acetyl group, a propionyl group, a butyryl group, an isobutyryl group, a valeryl group, an acrylyl group, a methacryloyl group, a KUROTO noil group, a KANHO roil group, benzoyl, an attereau POIRU group, a cinnamoyl group, a

furoyl group, a nicotinoyl group, etc. can be illustrated to a steel plate. Although these are united and R^7 and R^8 may form a part of cyclic structure, as an example of the cyclic structure, Cycloalkane or cycloalkene rings, such as a cyclohexane ring, a cyclohexene ring, a cyclopentane ring, and a cyclopentene ring, can be mentioned.
[0011]In the above-mentioned general formula (3), as Ln, a lantern (La), cerium (Ce), Neodium (Nd), samarium (Sm), a europium (Eu), Lanthanoids atoms, such as GATORINIUMU (Gd), praseodymium (Pr), dysprosium (Dy), holmium (Ho), erbium (Er), a thulium (Tm), an ytterbium (Yb), and lutetium (Lu), can use it conveniently. Perfluoro-alkyl groups, for example, a thing etc. which make a perfluoro-alkoxy group to a side chain of polymer like Nafion resin, such as a trifluoromethyl group, a pentafluoroethyl group, and a nonafluorobutyl group, can be mentioned as an example of R_f.
[0012]Silyl enol ether (1) shown by the above-mentioned general formula (1) is a following general formula (5).
[Formula 7]



(5)

alpha-hydronalium carbonyl compound expressed with (however, the inside of a formula, R^1, R^2, and R^3 are the same as the above), and a following general formula (6)
$XSiR^4R^5R^6$ (6)
It can manufacture easily by a publicly known method from a halo silane expressed with (however, X are a halogen atom among a formula and R^4, R^5, and R^6 are the same as the above). [For example, aI.Fleming, I.Paterson, Synthesis, 1979, p736;bH.O.House et al., J.Org.Chem., 34, p2324 (1969) reference] .
[0013]An oxidation lanthanoids to which a lanthanoid series catalyst shown by a general formula (3) is also equivalent (Ln_2O_3: among a formula) Ln can be easily manufactured by a publicly known method with it being the same as the above from perfluoro-alkane sulfonic acid (R_fSO_3H: the inside of a formula and R_f are the same as the above). [aJ.H.Forsberg et al., J.Org.Chem., 52, and p1017(1987);bM.-C.Almasio et al., Helv.Chim, Acta, 66, p1296 (1983) reference] .
[0014]When carrying out a reaction of this invention, silyl enol ether (1) and a carbonyl compound (2) do not usually interfere, even if **** for the amount of stoichiometries, i.e., equimolecular amounts, uses one side superfluously. When a compound which is especially one side is cheap, and a carbonyl compound (2) uses this superfluously, for example case [like formaldehyde], reaction velocity becomes quick and is preferred.
[0015]moreover -- the amount of said lanthanoid series catalyst (3) used in a reaction of this invention receives silyl enol ether (1) -- 0.1 - 200-mol% -- desirable -- 0.5 - 100-mol% -- they are 5 - 10-mol% more preferably. When there is less amount used than 0.1-mol%, a reaction does not advance substantially [reaction velocity is slow and], and a direction of a side reaction which is not liked has priority, and silyl enol ether (1) of a raw material may be consumed vainly. On the other hand, even if it uses a lanthanoid series catalyst (3) in large quantities exceeding the above-mentioned 200-mol%, it does not interfere, but since reaction velocity does not improve substantially, an economical advantage does not have it.
[0016]Although a non-solvent can also perform a reaction of this invention, it is good to carry out in a solvent preferably. And as a solvent to be used, any of a protic solvent and an aprotic

solvent may be sufficient. As an aprotic solvent, for example Dichloromethane, chloroform, Halogenated hydrocarbon, such as a dichloroethane, chlorobenzene, and dichlorobenzene, Ether system compounds, such as diethylether, a tetrahydrofuran, dimethoxyethane, and a jig lime, Aliphatic series or alicyclic hydrocarbon like hexane and cyclohexane, Although what is called aprotic polar solvents, such as aromatic hydrocarbon, such as benzene, toluene, and xylene, dimethylformamide, dimethylacetamide, dimethylimidazo RIJION, dimethyl sulfoxide, hexamethylphosphoric triamide, acetonitrile, etc. can use it extensively, An ether system compound and an aprotic polar solvent are preferred at a point that solubility to a raw material or a catalyst is high. As a protic solvent, lower alcohol, such as water, methanol, ethanol, and isopropyl alcohol, is preferred. These protic solvents are advantageous when performing what is called hydroxymethylation, using formaldehyde as said carbonyl compound (2). Water is especially the optimal as a solvent of this invention at a point that a reaction advances smoothly since it is easy to melt a lanthanoid series catalyst (3) in addition to this advantage, and a point that recovery of a lanthanoid series catalyst (3) and a reuse become easy like the after-mentioned. When using water as a solvent, it is good to use as a mixed solvent system with ethanol, a tetrahydrofuran, dimethylformaldehyde, etc. which can be mixed as easily [it is desirable and] as this, and, thereby, solubility's over silyl enol ether (1) improves.
[0017]Although reaction temperature changes also with reactional solvents and catalyst amounts to be used, a range of it is usually -100-150 **, and a range of it is 10-80 ** preferably 0-150 ** in a protic solvent. Although reaction time also changes with reaction conditions, a reaction is usually ended in 10 minutes - 50 hours.
[0018]By the way, although a resultant of this invention is an aldol compound expressed with said general formula (4), when a non-solvent or an aprotic solvent is used, in a general formula (4), a compound whose Z is $-SiR^4R^5R^6$ is obtained as a main output. By processing this compound in a weak alkaline aqueous solution or weak acidic solution, it is hydrolyzed easily and Z becomes a compound which is a hydrogen atom in a general formula (4). When a reactional solvent is a protic solvent, a compound whose Z is hydrogen directly is obtained.
[0019]After ending reaction, although the target aldol compound (4) can be easily isolated by carrying out post-processing of the reaction mixture by various methods, a method shown below is preferred at especially a point that can collect lanthanoid series catalysts (3) easily and can carry out a reuse. That is, after adding water of the amount of solvents to a reaction mixture, an aldol compound (4) is separated from solution with a solvent extraction method etc. In particular when a reactional solvent is water, it is not necessary to add water. Thus, if this aldol compound (4) after separating an aldol compound (4) from a reaction mixture is necessary in accordance with a conventional method, after it will perform hydrolysis treatment further, it is refined by methods, such as column chromatography, distillation, and recrystallization. On the other hand, since it is dissolving into solution, a lanthanoid series catalyst (3) isolates as a residue by carrying out heating distilling off of the water, if necessary, will perform refining operation further and will carry out a reuse as a reaction catalyst of this invention. When reacting this invention in an aqueous solvent, in a reaction of this invention performed to the next as it is without isolating, the reuse of the lanthanoid series catalyst (3) can be carried out as a catalyst from this solution.
[0020]
[Function]It is thought that the lanthanoid series catalyst (3) used by this invention is functioning as what is called a Lewes acid catalyst. And unlike the case of the Lewes acid catalyst known conventionally, the feature is in the point which maintains activity without decomposing also in a

protic solvent, and the point of melting into water well. For this reason, into a protic solvent, this invention can be reacted suitably, if it is not among a protic solvent, it will be easy to polymerize by this, and it can be used as a carbonyl compound (2) also about unstable formaldehyde, and a good result is obtained. Since a lanthanoid series catalyst (3) melts well for not decomposing even if it touches water, separation with output becomes easy and catalyst reuse can be conjointly performed simple with a point with a reaction of this invention feasible about also in a protic solvent.

[0021]

[Example]Hereafter, based on an example, this invention is explained still in detail.

[0022]It mixes at a room temperature under stirring of 1 ml (37% of formaldehyde and 8 to 10% of methanol are contained) of formaldehyde solutions and 3 ml of tetrahydrofurans of example 1 marketing, and is a tris(trifluoromethanesulfonic acid) ytterbium to this. [$Yb(OSO_2CF_3)_3$] 0.4 mmol/1 ml of tetrahydrofuran solutions of 0.04mmol and a 1-phenyl-1-trimethylsilyloxy 1-propene were added one by one, and it stirred at the temperature for 24 hours. Subsequently, after distilling off a tetrahydrofuran under decompression, 10 ml of water was added and dichloromethane extracted (5 ml x 3 times). After rinsing the obtained extract (10mlx3) and drying (Na_2SO_4), It condensed under decompression, column chromatography (silica gel, hexane-ethyl acetate) refined the residue, and 61.7 mg (94% of yield) of 3-hydroxy-2-methyl-1-phenyl-1-propanone of the resultant was obtained as transparent oil. IR, NMR, MS, etc. were measured about the acquired resultant. A result is shown in Table 1 and 2.

[0023]It replaces with Example 2 - a 101-phenyl-1-trimethylsilyloxy 1-propene, and various silyl enol ether (1) was used and was made to react like Example 1. The silyl enol ether (1) used here, the acquired resultant, and yield are shown in Table 1. Results, such as IR, NMR, MS, etc. which were measured like Example 1 about the aldol compound (4) of the acquired resultant, are shown in Table 2 - 4.

[0024]A 1-phenyl-1-trimethylsilyloxy 1-propene is used as 11 to example 20 silyl enol ether (1), as opposed to this silyl enol ether (1) -- $Yb(OSO_2CF_3)_3$ or other lanthanoid series catalysts (3) of various kinds of -- respectively -- 100-mol% -- it was used and was made to react like Example 1 The kind of lanthanoid series catalyst (3) used here and the obtained yield of the aldol compound (4) of a resultant are shown in Table 5.

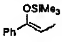
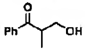
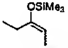
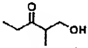
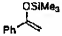
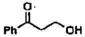
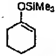
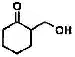
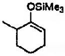
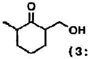
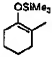
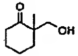
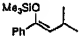
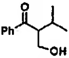
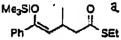
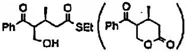
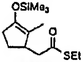
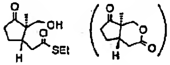
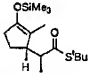
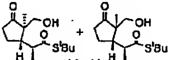
[0025]It reacted completely like the above-mentioned Examples 11-20 except having carried out 21 to example 30 reaction time in 1 hour. The yield of the aldol compound (4) of the resultant at this time is shown in Table 6.

[0026]It reacted completely like the above-mentioned Examples 11-20 except having carried out 31 to example 40 catalyst amount, and having made reaction time into 36 hours 20-mol%. The yield of the aldol compound (4) of the resultant at this time is shown in Table 7.

[0027]$Yb(OSO_2CF_3)_3$ is used as Example 41 - a 43 lanthanoid-series catalyst (3), It reacted completely like the above-mentioned Example 1 except having made the amount of $Yb(OSO_2CF_3)_3$ used to a 1-phenyl-1-trimethylsilyloxy 1-propene into 5-mol% and 1-mol% 10-mol%, respectively. The yield of the aldol compound (4) of the resultant at this time is written together to Table 7.

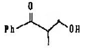
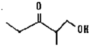
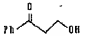
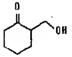
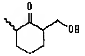
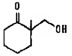
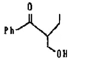
[0028]In the reaction of example 44 Example 1, vacuum concentration of 10 ml of the solution after dichloromethane extracts a reaction mixture was carried out. 1 ml of commercial formaldehyde and a mixture with 3 ml of tetrahydrofurans were added to the residue, and also 0.4 mmol/1 ml of tetrahydrofuran solutions of the 1-phenyl-1-trimethylsilyloxy 1-propene were added, and it was made to react under stirring at a room temperature for 24 hours. The same

post-processing as Example 1 was performed after ending reaction, and 59.7 mg (91% of yield) of 3-hydroxy-2-methyl-1-phenyl-1-propane was obtained. Under the present circumstances, 1 ml of solution after dichloromethane extracts a reaction mixture is used as a catalyst of the reaction of formaldehyde and a 1-phenyl-1-trimethylsilyloxy 1-propene by the again same operation as the above, The same reaction as the above was performed, and also 61.0 mg (93% of yield) of 3-hydroxy-2-methyl-1-phenyl-1-propanone was obtained.
[0029]In example 45 Example 1, replace with 1 ml of formaldehyde solutions, and a mixture with 3 ml of tetrahydrofurans, and (E)-2-hexanal 0.4mmol, 3 ml of tetrahydrofurans, and the mixture of 1 ml of water are used, Replaced with the 1-phenyl-1-trimethylsilyloxy 1-propene, used the 1-trimethylsilyloxy 1-cyclohexene, it was made to react at a room temperature for 19 hours, same post-processing, separation, and refining were performed, and the aldol compound (4) of the resultant was obtained. Results, such as IR, NMR, MS, etc. which were measured like Example 1 about the acquired resultant, are shown in Table 4. The kind of silyl enol ether (1) and carbonyl compound (2), reaction time, and yield which were used for the reaction are shown in Table 8.
[0030]It replaces with 1 ml of formaldehyde solutions, and a mixture with 3 ml of tetrahydrofurans in 46 to example 48 Example 1, Used acrolein 0.4mmol, acetaldehyde 0.4mmol, or chloroacetaldehyde 0.4mmol, it was made to react similarly, and the aldol compound (4) of the resultant was obtained. Results, such as IR, NMR, MS, etc. which were measured like Example 1 about the acquired resultant, are shown in Table 4. The kind of silyl enol ether (1) and carbonyl compound (2), reaction time, and yield which were used for the reaction are shown in Table 8.
[0031]
[Table 1]

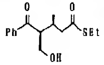
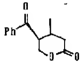
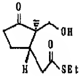
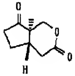
実施例 No.	シリルエノールエーテル（1）	反応生成物	収率（%）
1	 a		94
2	 b		85
3			77
4			82
5		 (3:2)	86
6			92
7	 a		92
8	 a	 c	88
9		 d	83
10		 (6:1)	90

（注） Me:メチル基、Ph: フェニル基、Et: エチル基、 ᵗBu: t-ブチル基、
a): Z/E = >98/2、b): Z/E = 1:4 、c): ラクトンとの 2:1混合物、
d): ラクトンとの 3:1混合物

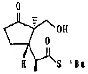
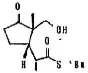
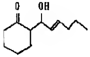
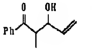
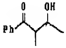
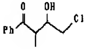
[0032]
[Table 2]

実施例	生成物	同定データまたはデータ掲載文献（既知化合物）
1.		IR(neat): 3420, 1674cm^{-1}; ^{1}H NMR($CDCl_3$) δ: 1.24(d,3H,J=7.6Hz), 2.38(brs,1H), 3.63-4.02(m,3H), 7.45-7.62(m,3H), 7.95-7.99(m,2H)
2.		IR(neat): 3420, 1730cm^{-1}; ^{1}H NMR($CDCl_3$) δ: 1.06(t,3H,J=7.3Hz), 1.13(d,2H,J=7.3Hz), 2.40-2.63(m,3H), 2.72-2.83(m,1H), 3.66(dd,J=11.0,5.3Hz), 3.75(dd,J=11.0,5.3Hz)
3.		IR(neat): 3420, 1674cm^{-1}; ^{1}H NMR($CDCl_3$) δ: 2.73(brs,1H), 3.23(t,J=5.3Hz), 4.04(t,J=5.3Hz), 7.44-7.62(m,3H), 7.95-7.99(m,2H)
4.		Tetrahedron, 44, 6065(1988)
5.		J. Am. Chem. Soc., 112, 7422(1990)
6.		J. Am. Chem. Soc., 112, 7422(1990)
7.		IR(neat): 3420, 1674cm^{-1}; ^{1}H NMR($CDCl_3$) δ: 0.95(d,6H,J=6.6Hz), 2.19(dq,1H,J=7.6,6.6Hz), 2.19(brs,1H), 3.48(ddd,1H,J=7.6,7.6,3.3Hz), 3.83(dd,1H,J=10.9,3.3Hz), 4.06(dd,1H,J=10.9,7.6Hz), 7.41-7.59(m,3H), 7.94-7.98(m,2H); ^{13}C NMR($CDCl_3$) δ: 19.7, 21.4, 28.6, 54.1, 61.3, 128.4, 128.7, 133.3, 137.8, 205.3; m/z: 192.1145, calcd. for $C_{12}H_{16}O_2$ 192.1148

[0033]
[Table 3]

実施例	生成物	同定データまたはデータ掲載文献（既知化合物）
8．		IR(neat): 3475, 1732, 1674cm $^{-1}$; ^{1}H NMR(CDCl$_3$) δ : 0.96(d,3H,J=6.9Hz), 1.25(t,3H,J=7.4Hz), 2.26(brs,1H), 2.46-2.57(m,1H), 2.62-2.80(m,1H), 2.89(q,2H,J=7.4Hz), 3.73(ddd,1H,J=6.9,4.3,4.0Hz), 3.83(dd,1H,J=11.2,4.0Hz), 4.08(dd,1H,J=11.2,6.9Hz), 7.42-7.62(m,3H), 7.98-8.01(m,2H); ^{13}C NMR(CDCl$_3$) δ : 14.8, 16.5, 23.5, 30.8, 48.5, 51.2, 60.2, 128.5, 128.8, 133.5, 136.7, 198.8, 203.6; m/z: 280.1130, calcd. for: $C_{15}H_{20}O_3S$ 280.1131
		IR(neat): 1741, 1674cm^{-1}; ^{1}H NMR(CDCl$_3$) δ : 1.07(d,3H,J=6.6Hz), 2.31(dd,1H,J=16.8,8.3Hz), 2.58-2.74(m,1H), 2.86(dd,1H,J=16.8,7.6Hz), 3.63(ddd,1H,J=9.6,8.1,5.3Hz), 4.36(dd,1H,J=11.5,9.6Hz), 4.49(dd,1H,J=11.5,5.3Hz), 7.49-7.67(m,3H), 7.95-7.99(m,2H); ^{13}C NMR(CDCl$_3$) δ : 20.8, 29.6, 36.7, 47.7, 69.2, 128.4, 129.1, 134.1, 136.2, 170.6, 198.9; m/z: 218.0945, calcd. for: $C_{13}H_{14}O_3$ 218.0942
9．		IR(neat): 3460, 1734, 1687cm^{-1}; ^{1}H NMR(CDCl$_3$) δ : 0.84(s,3H), 1.27(t,3H,J=7.4Hz), 2.11-2.85(m,7H), 2.91(q,2H,J=7.4Hz), 3.39(d,1H,J=11.2Hz), 3.70(d,1H,J=11.2Hz); ^{13}C NMR(CDCl$_3$) δ : 13.7, 14.6, 23.5, 24.9, 37.2, 37.3, 44.4, 52.8, 65.2, 198.8, 222.0; m/z: 230.0965, calcd. for: $C_{11}H_{18}O_3S$ 230.0974
		IR(neat): 1741, 1737cm^{-1}; ^{1}H NMR(CDCl$_3$) δ : 1.13(s,3H), 1.57-1.67(m,1H), 2.28-2.59(m,5H), 2.74-2.83(m,1H), 3.93(d,1H,J=11.5Hz), 4.39(d,1H,J=11.5Hz); ^{13}C NMR(CDCl$_3$) δ : 21.2, 26.4, 34.0, 36.8, 39.1, 47.2, 71.7, 172.1, 218.9; m/z: 168.0787, calcd. for: $C_9H_{12}O_3$ 168.0785

[0034]
[Table 4]

実施例	生成物	同定データまたはデータ掲載文献（既知化合物）
10.		IR(neat): 3465, 1734, 1678cm^{-1}; ^{1}H NMR(CDCl$_3$) δ: 0.84(s,3H), 1.25(d,3H,J=6.8Hz), 1.48(s,9H), 2.11-2.22(m,2H), 2.35-2.45(m,1H), 2.58-2.67(m,3H), 3.22(d,1H,J=9.9Hz), 3.77(dd,1H,J=10.2,9.9Hz); ^{13}C NMR(CDCl$_3$) δ: 14.1, 17.8, 22.8, 29.5, 36.7, 41.1, 48.4, 49.3, 53.6, 65.0, 205.5, 221.3; m/z: 272.1442, calcd. for: $C_{14}H_{24}O_3S$ 272.1444
		IR(neat): 3465, 1734, 1678cm^{-1}; ^{1}H NMR(CDCl$_3$) δ: 0.98(s,3H), 1.23(d,3H,J=6.6Hz), 1.48(s,9H), 1.67-1.78(m,3H), 2.04-2.46(m,3H), 2.84-2.92(m,1H), 3.76(dd,1H,J=8.9,5.0Hz), 3.82(d,1H,J=8.9Hz); ^{13}C NMR(CDCl$_3$) δ: 17.7, 20.5, 24.7, 29.7, 37.4, 48.2, 48.7, 49.2, 52.5, 66.1, 204.0, 223.9
45.		IR(neat): 3450, 1730cm^{-1}; ^{1}H NMR(CDCl$_3$) δ: 0.8-2.8(m,15H), 3.10(brs,1H), 3.90-4.50(m,1H), 5.05-5.90(m,2H)
46.		IR(neat): 3450, 1676cm^{-1}; ^{1}H NMR(CDCl$_3$) δ: 1.21-1.27(m,3H), 3.00(d,1H), 3.22(s,1H), 3.50-3.63(m,1H), 4.40(d,0.6H), 4.60(d,0.4H), 5.18-5.40(m,2H), 5.82-5.99(m,1H), 7.43-7.64(m,3H), 7.91-7.97(m,2H)
47.		IR(neat): 3450, 1676cm^{-1}; ^{1}H NMR(CDCl$_3$) δ: 1.21-1.29(m,6H), 2.95(s,0.46H), 3.18(s,0.54H), 3.38-3.54(m,1H), 4.08-4.29(m,1H), 7.44-7.62(m,3H), 7.93-7.99(m,2H)
48.		IR(neat): 3448, 1676cm^{-1}; ^{1}H NMR(CDCl$_3$) δ: 3.15(brs,1H), 3.61(d,0.9H), 3.63(d,1.1H), 4.13(dd,1H), 4.25(dd,1H), 7.46-7.63(m,3H), 7.95-8.00(m,2H)

[0035]
[Table 5]

実施例 No.	Ln（OTf）$_3$	シリルエノールエーテル(1)に対する触媒量（mol%）	反応時間（h）	アルドール化合物の収率（%）
11	La（OTf）$_3$	100	24	90
12	Pr（OTf）$_3$	〃	〃	92
13	Nd（OTf）$_3$	〃	〃	74
14	Sm（OTf）$_3$	〃	〃	92
15	Eu（OTf）$_3$	〃	〃	92
16	Gd（OTf）$_3$	〃	〃	92
17	Dy（OTf）$_3$	〃	〃	89
18	Ho（OTf）$_3$	〃	〃	91
19	Er（OTf）$_3$	〃	〃	90
20	Yb（OTf）$_3$	〃	〃	94

（注）式中、Tfは$-SO_2CF_3$を示す。

[0036]
[Table 6]

実施例 No.	Ln（OTf）$_3$	シリルエノールエーテル(1)に対する触媒量（mol%）	反応時間（h）	アルドール化合物の収率（%）
21	La（OTf）$_3$	100	1	23
22	Pr（OTf）$_3$	〃	〃	40
23	Nd（OTf）$_3$	〃	〃	6
24	Sm（OTf）$_3$	〃	〃	51
25	Eu（OTf）$_3$	〃	〃	28
26	Gd（OTf）$_3$	〃	〃	20
27	Dy（OTf）$_3$	〃	〃	20
28	Ho（OTf）$_3$	〃	〃	38
29	Er（OTf）$_3$	〃	〃	44
30	Yb（OTf）$_3$	〃	〃	5

（注）式中、Tfは$-SO_2CF_3$を示す。

[0037]

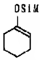
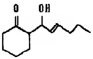
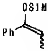
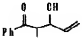
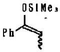
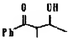
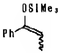
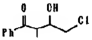
[Table 7]

実施例 No.	Ln(OTf)$_3$	ｼﾘﾙｴﾉｰﾙｴｰﾃﾙ(1)に対する触媒量(mol%)	反応時間(h)	ｱﾙﾄﾞｰﾙ化合物の収率(%)
31	La(OTf)$_3$	20	36	88
32	Pr(OTf)$_3$	〃	〃	80
33	Nd(OTf)$_3$	〃	〃	89
34	Sm(OTf)$_3$	〃	〃	91
35	Eu(OTf)$_3$	〃	〃	93
36	Gd(OTf)$_3$	〃	〃	79
37	Dy(OTf)$_3$	〃	〃	85
38	Ho(OTf)$_3$	〃	〃	86
39	Er(OTf)$_3$	〃	〃	83
40	Yb(OTf)$_3$	〃	〃	94
41	〃	10	24	94
42	〃	5	24	90
43	〃	1	24	90

(注)式中、Tfは$-SO_2CF_3$を示す。

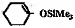
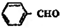
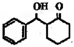
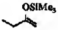
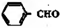
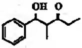
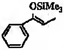
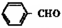
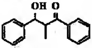
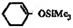
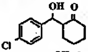
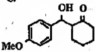
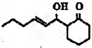
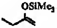
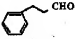
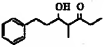
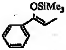
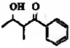
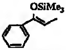
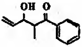
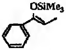
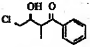
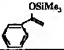
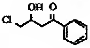
[0038]

[Table 8]

実施例 No.	ｼﾘﾙｴﾉｰﾙｴｰﾃﾙ ｴｰﾃﾙ (1)	ｶﾙﾎﾞﾆﾙ 化合物 (2)	反応生成物 (4)	反応時間 (h)	収率 (%)
45				19	90
46				44	82
47		CH_3CHO		30	93
48		$ClCH_2CHO$		39	95

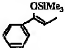
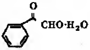
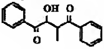
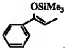
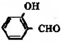
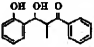
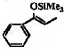
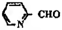
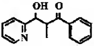
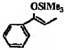
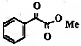
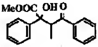
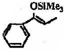
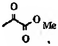
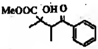
[0039]Tris(trifluoromethanesulfonic acid) ytterbium 0.04mmol is dissolved in 1.0 ml of example 49 tetrahydrofurans, and the mixed solution of 0.5 ml of water, The solution which made 1 ml of tetrahydrofurans dissolve benzaldehyde 0.4mmol and 1-phenyl-1-trimethylsilyloxy 1-propene 0.44mmol in this mixed solution was added at the room temperature, and was made to react under 20-hour stirring at the temperature. Subsequently, after distilling off a tetrahydrofuran under decompression, add 10 ml of water and dichloromethane extracts (5 ml x 3 times), The obtained extract was rinsed (10 ml x 3 times), and it dried (Na_2SO_4), and condensed under decompression, column chromatography (silica gel, hexane-ethyl acetate) refined the residue, and the aldol compound which is a resultant was obtained with 91% of yield. IR, NMR, MS, etc. were measured about the acquired resultant. A result is shown in Table 9 and 11.
[0040]Various lanthanoid series catalysts which replace with Example 50 - 62 tris(trifluoromethanesulfonic acid) ytterbium, and are expressed with a general formula (3) are used, Various carbonyl compounds which replace with benzaldehyde and are expressed with a general formula (2) are used, Except having used the silyl enol ether which replaces with a 1-phenyl-1-trimethylsilyloxy 1-propene, and is expressed with a general formula (1), it was made to react like the above-mentioned Example 49, and the aldol compound of the resultant expressed with a general formula (4) was obtained. About the acquired resultant, IR, NMR, MS, etc. were measured like Example 49. A result is shown in Tables 9-13.
[0041]Various carbonyl compounds which replace with 63 to example 64 benzaldehyde, and are expressed with a general formula (2) are used, The same operation as the above-mentioned Example 49 was performed, and it was made to react at a room temperature for 40 hours except having used the silyl enol ether which replaces with a 1-phenyl-1-trimethylsilyloxy 1-propene, and is expressed with a general formula (1). Then, operation of the same post-processing as Example 49, separation, and refining was performed, and the aldol compound of the resultant expressed with a general formula (4) was obtained. About the acquired resultant, IR, NMR, MS, etc. were measured like Example 49. A result is shown in Table 10 and 13.
[0042]Except having replaced with 1.0 ml of tetrahydrofurans and the mixed solvent of 0.5 ml of water in which example 65 tris(trifluoromethanesulfonic acid) ytterbium 0.04mmol is dissolved, and having used 1.5 ml of tetrahydrofurans, Like the above-mentioned Example 49, each operation of a reaction, post-processing, separation, and refining was performed, and the aldol compound of the resultant expressed with a general formula (4) was obtained. A result is shown in Table 14.
[0043]It replaces with 1.0 ml of tetrahydrofurans and the mixed solvent of 0.5 ml of water in which Example 66 - 68 tris(trifluoromethanesulfonic acid) ytterbium 0.04mmol are dissolved, 1.5 ml of dichloromethane, 1.5 ml of acetonitrile, or 1.5 ml of dimethylformamide is used, respectively, It replaces with 1 ml of tetrahydrofurans in which benzaldehyde 0.4mmol and 1-phenyl-1-trimethylsilyloxy 1-propene 0.44mmol are dissolved, Except having used 1.0 ml of dichloromethane, 1.0 ml of acetonitrile, or 1.0 ml of dimethylformamide, respectively, like the above-mentioned Example 49, each operation of a reaction, post-processing, separation, and refining was performed, and the aldol compound of the resultant expressed with a general formula (4) was obtained. A result is shown in Table 14.
[0044]Various lanthanoid series catalysts which replace with the tris(trifluoromethanesulfonic acid) ytterbium used in 69 to example 79 Example 49, and are expressed with a general formula (3) are used, Like Example 49, each operation of a reaction, post-processing, separation, and refining was performed, and the aldol compound of the resultant expressed with a general formula (4) was obtained. A result is shown in Table 15.

[0045]
[Table 9]

実施例 No.	シリルエノールエーテル(1)	カルボニル化合物(2)	ランタノイド系触媒（3）	反応生成物(4)	収率(%)
49			Yb(OTf)$_3$		91
50			Yb(OTf)$_3$		93
51			Yb(OTf)$_3$		81
52			Yb(OTf)$_3$		89
53			Yb(OTf)$_3$		77
54			Yb(OTf)$_3$		90
55			Yb(OTf)$_3$		79
56		CH_3CHO	Gd(OTf)$_3$		93
57			Gd(OTf)$_3$		82
58			Yb(OTf)$_3$		95
59			Yb(OTf)$_3$		67

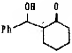
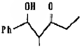
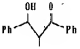
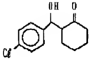
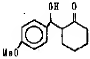
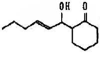
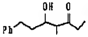
（注）式中、Ｔｆは$-SO_2CF_3$を示す。

[0046]
[Table 10]

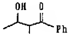
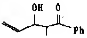
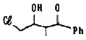
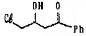
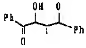
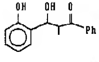
実施例No.	シリルエノールエーテル(1)	カルボニル化合物(2)	ランタノイド系触媒（3）	反応生成物(4)	収率(%)
60			Yb(OTf)3		67
61			Lu(OTf)3		81
62			Lu(OTf)3		87
63			Yb(OTf)3		68
64			Yb(OTf)3		79

(注) 式中、Ｔｆは－SO_2CF_3を示す。

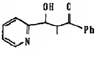
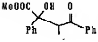
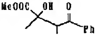
[0047]
[Table 11]

実施例	生成物	同定データまたはデータ掲載文献（既知化合物）
49.		Chem. Pharm. Bull., 38(6), 1509-1512(1990)
50.		Chem. Lett., 1535(1985)
51.		Chem. Pharm. Bull., 38(6), 1509-1512(1990)
52.		同上
53.		同上
54.		IR(neat): 3464, 1703cm^{-1}; ^{1}H-NMR($CDCl_3$) δ : 0.90(t, 3H, J=7.26Hz), 1.23-2.50(m, 13H), 2.60-3.00(brs, 1H), 4.43-4.51(m, 1H), 5.43-5.51(m, 1H), 5.63-5.74(m, 1H); ^{13}C-NMR($CDCl_3$) δ : 13.6, 22.2, 24.7, 27.3, 27.5, 34.3, 42.5, 55.6, 70.8, 129.2, 132.6, 214.4;
55.		IR(neat): 3458, 1705cm^{-1}; ^{1}H-NMR($CDCl_3$) δ : 0.99-1.15(m, 6H), 1.53-1.91(m, 2H), 2.35-2.94(m, 6H), 3.63-3.69[m, 1H(anti)], 3.90-3.93[m, 1H(syn)], 7.17-7.30(m, 5H); ^{13}C-NMR($CDCl_3$) δ : 7.5, 10.1, 32.2, 49.9, 70.4, 125.8, 128.4, 141.8, 216.5(syn), 7.4, 14.1, 31.9, 51.0, 73.0, 125.8, 128.3, 141.9, 216.7(anti)

[0048]
[Table 12]

実施例	生成物	同定データまたはデータ掲載文献（既知化合物）
56.		IR(neat): 3460, 1676cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ : 1.21-1.29(m, 3H), 2.95[brs., 1H(anti)], 3.13[brs., 1H(syn)], 3.38-3.54(m, 1H), 4.06-4.16[m, 1H(anti)], 4.20-4.29[m, 1H(syn)], 7.44-7.62(m, 3H), 7.93-7.99(m, 2H); ^{13}C-NMR(CDCl$_3$) δ : 11.2, 20.3, 45.8, 67.4, 128.4, 128.7, 133.4, 135.9, 205.8(syn); 15.2, 20.7, 47.7, 69.8, 128.3, 128.6, 133.3, 136.5, 205.3(anti);
57.		^{1}H-NMR(CDCl$_3$) δ : 1.22[d, 3H(anti), J=7.26Hz], 1.26[d, 3H(syn), J=6.93Hz], 3.01[brs., 1H(anti)], 3.23[brs., 1H(syn)], 3.50-3.66(m, 1H), 4.38-4.43[m, 1H(anti)], 4.58-4.60[m, 1H(syn)], 5.17-5.40(m, 2H), 5.82-5.99(m, 1H), 7.43-7.61(m, 3H), 7.90-7.97(m, 2H);
58.		IR(neat): 3423, 1676cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ : 1.27-1.32(m, 3H), 3.16[brs., 1H), 3.61-3.96(m, 1H), 4.11-4.17[m, 1H(anti)], 4.22-4.28[m, 1H(syn)], 7.46-7.63(m, 3H), 7.95-8.00(m, 2H); ^{13}C-NMR(CDCl$_3$) δ : 12.3, 42.4, 46.6, 71.8, 204.0(syn); 15.0, 42.2, 47.3, 73.5, 204.6(anti);
59.		IR(neat): 3454, 1678cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ : 3.29-3.32(dd, 2H), 3.49(brs., 1H), 3.69-3.71(dd, 2H), 4.44-4.52(m, 1H), 7.46-7.63(m, 3H), 7.95-7.98(m, 2H); ^{13}C-NMR(CDCl$_3$) δ : 42.0, 48.3, 67.8, 128.1, 128.7, 133.3, 136.4, 199.4;
60.		IR(neat): 3462, 1682, 1678cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ : 1.12(d, 3H, J=7.26Hz), 3.74(d, 1H, J=6.27Hz), 3.79-3.88(m, 1H), 5.47(dd, 1H): ^{13}C-NMR(CDCl$_3$) δ : 10.4, 44.7, 73.5, 128.2, 128.5, 128.6, 128.9, 133.1, 134.0, 200.3, 201.4;
61.		IR(neat): 3332, 1670cm $^{-1}$; ^{1}H-NMR(CDCl$_3$) δ : 1.03[d, 3H(anti), J=7.26Hz], 1.30[d, 3H(syn), J=7.25Hz), 3.73-3.82[m, 1H(anti)], 4.00-4.11[m, 1H(syn)], 4.82(brs., 1H), 5.11[d, 1H(anti), J=8.90Hz], 5.39[d, 1H(syn), J=3.30Hz], 6.79-7.69(m, 7H), 7.90-7.99(m, 2H), 8.13[brs., 1H(syn or anti)], 8.77[brs., 1H(syn or anti)];

[0049]
[Table 13]

実施例	生成物	同定データまたはデータ掲載文献（既知化合物）
62.		^{1}H-NMR(CDCl$_3$) δ : 1.16(d, 3H, J=7.26Hz), 4.04-4.13(m, 1H), 4.23(brs., 1H), 5.23(d, 1H, J=3.96Hz), 7.15-7.19(m, 1H), 7.42-7.70(m, 5H), 7.96(d, 2H, J=7.59Hz), 8.53-8.55(m, 1H); ^{13}C-NMR(CDCl$_3$) δ : 11.6, 46.2, 73.7, 121.3, 122.3, 128.5, 128.6, 133.3, 135.8, 136.6, 148.5, 160.6, 205.1;
63.		^{1}H-NMR(CDCl$_3$) δ : 1.04(d, 3H, J=7.59Hz), 3.64(s, 3H), 4.38(q, 1H), 5.12(s, 1H), 7.33-7.69(m, 8H), 8.02(d, 2H, J=7.26Hz); ^{13}C-NMR(CDCl$_3$) δ : 12.1, 48.1, 52.8, 80.3, 125.0, 127.9, 128.4, 128.6, 128.8, 133.8, 135.3, 138.8, 175.1, 207.2;
64.		^{1}H-NMR(CDCl$_3$) δ : 1.32[d, 1H(anti), J=7.26Hz], 1.39[d, 1H(syn), J=7.59Hz], 1.46[s, 3H(syn)], 1.50[s, 3H(anti)], 3.63[s, 3H(syn)], 3.81[s, 3H(anti)], 3.88-4.01(m, 1H), 4.06(s, 1H(anti)], 4.32[s, 1H(syn)], 7.46-7.63(m, 3H), 7.92-7.99(m, 2H); ^{13}C-NMR(CDCl$_3$) δ : 11.8, 23.4, 46.1, 52.4, 75.9, 176.7, 206.2(syn); 14.1, 25.1, 47.9, 52.6, 76.1, 175.5, 209.6(anti);

[0050]
[Table 14]

実施例 No.	反応溶媒	収率 (%)
65	テトラヒドロフラン	10.0
66	ジクロロメタン	10.0
67	アセトニトリル	5.0
68	ジメチルホルムアミド	56.0

[0051]
[Table 15]

実施例 No.	Ln(OTf)3	収率 (%)
69	La(OTf)3	8.0
70	Pr(OTf)3	28.0
71	Nd(OTf)3	83.0
72	Sm(OTf)3	46.0
73	Eu(OTf)3	34.0
74	Gd(OTf)3	89.0
75	Dy(OTf)3	73.0
76	Ho(OTf)3	47.0
77	Er(OTf)3	52.0
78	Tm(OTf)3	20.0
79	Lu(OTf)3	88.0

(注) 式中、Ｔｆは－ＳＯ₂ＣＦ₃を示す。

[0052]
[Effect of the Invention]this invention method enables application of the high alternative aldol condensation reaction developed in recent years about the extensive carbonyl compound which also contains difficult formaldehyde in the former.
The catalysts used in that case can be collected easily, a reuse can be carried out, and practical value is industrially large.